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Monitoring of Neonicotinoid Pesticides in Water-Soil Systems Along the Agro-Landscapes of the Cauvery Delta Region, South India

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Abstract

The prophylactic use of neonicotinoids in paddy fields has raised concern due to its toxicity to ecological systems and human health. The present study evaluated the concentrations of neonicotinoids such as clothianidin, imidacloprid, thiamethoxam, acetamiprid, and thiacloprid in the water-soil systems of the paddy fields, and their potential discharge into the groundwater along the Cauvery delta region, South India. Though neonicotinoids are extensively sprayed in the paddy fields, the concentration of residues analyzed by QuEChERS, combined with LC–MS/MS found no detectable residues at concentrations above LOD. The LOD and the LOQ values for water and soil were 0.001 ppm and 0.0025 ppm and 0.025 ppm and 0.05 ppm respectively. The results of the study found that neonicotinoids are less persistent in the water-soil systems of the delta region as they are readily exposed to photolysis and undergo rapid microbial degradation. Further, the hydropedological characteristics of the highly saturated delta soil facilitate ready leaching followed by vertical migration and infiltration into the soil aquifers.

Keywords Neonicotinoids · QuEChERS · Hydropedological · Leaching · Infiltration

The prophylactic use of neonicotinoid pesticides in paddy fields against a wide range of pests has raised concern due to its toxicity to the water-soil systems, environment, and human health. Among neonicotinoids, imidacloprid, clothianidin, acetamiprid, thiamethoxam, and thiacloprid are widely popular (Zhang et al. 2019) of which, imidacloprid is highly toxic to the non-target groups (Cox 2001). Though these pesticides are neurotoxic, they are extensively sprayed through the different stages of plant growth (Sattler et al. 2018). Agricultural activities including seed treatments, sprays, irrigation systems (Elbert et al. 2008), and agricultural runoff are the dispersion sources of neonicotinoids into the environment and the surrounding water-soil systems (Jurado et al. 2019). Neonicotinoids are highly water-soluble (Wood and Goulson 2017; Reynoso et al. 2019) and their absorption and degradation depend on various hydropedological characteristics of the soil such as pH, ambient temperature, texture, moisture, organic carbon, and organic matter (Karmakar 2006; Bonmatin et al. 2015; Pietrzak et al. 2020). Among the soil types, loamy soil exhibits maximum retention followed by clay and sandy soil (Mortl et al. 2016; Leiva et al. 2017). Warmer regions have reported higher pesticide degradation with increasing temperatures (Hooper et al. 2013) whereas, colder regions showed slower degradation. Numerous studies have raised concerns over the toxicity levels of neonicotinoids in the soil (Schaafsma et al. 2015; Limay-Rios et al. 2016), water (Morrissey et al. 2015; Benton et al. 2016), and in different levels of organisms (Rundlof et al. 2015; Chan et al. 2019; Holtswarth et al. 2019; Gunalet al. 2020). The extensive use of these pesticides has also affected the provisioning of vital ecosystem services by birds and bees thus affecting crop production. (Chagnon et al. 2015). Neonicotinoids are widely used in rice cultivation and paddy being the principal crop of the delta, are highly exposed to these insecticides than other food crops cultivated along this delta belt.

The Cauvery delta region is widely known as "Nerkalanchiyam", the land of paddy cultivation, and also as the 'rice bowl' of South India. The rice grown along the Cauvery delta zone belongs to the traditional varieties. The major part of the basin is covered by agricultural land

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accounting for 66.21% of the total area and 4.09% of the basin is covered with aquatic bodies. There are limited field studies on neonicotinoids along the Cauvery delta region under realistic agricultural conditions, and there still exist knowledge gaps on the impacts of exposure. The present study will help in evaluating the concentration of neonicotinoids in water-soil systems in the paddy fields along the delta region and their discharge into the groundwater under realistic agricultural conditions. We hypothesize that the hydropedological characteristic of the highly saturated delta soil reduces the persistence of detectable neonicotinoid residues in the water-soil systems in the paddy fields.

Materials and Methods

A total of 12 samples (six soil and six water samples) were collected and analyzed from the regions of Kallanai, Thiruvaiyaru, Needmanagalam, and Mannargudi along the Cauvery delta region, South India (Fig. 1). Upon immediate transportation to the laboratory, the samples were stored at − 20°C. The analytical standards of neonicotinoids including clothianidin, imidacloprid, thiamethoxam, acetamiprid, and thiacloprid were purchased from Dr. Erhenstorfer, Germany. Standard stock solutions (400 µg/mL) were prepared by dissolving a weighed quantity of technical-grade material in LC–MS grade acetonitrile (50:50). The stock solutions were diluted to prepare an intermediate stock solution (40 µg/mL) and the working standards by diluting the intermediate stock solution. The extraction and clean-up procedures were done following the QuEChERS method (Anastassiades et al. 2003).

For soil analysis, 10 g soil was transferred to a 50 mL centrifuge tube containing 20 ml acetonitrile and briefly vortexed for 1 min. To this, 4 g anhydrous magnesium sulfate and 1 g sodium chloride were added, and again vortexed for 1 min. After centrifugation for 6000 rpm for 10 min, 9 mL of clear supernatant was transferred to a new centrifuge tube containing 100 mg Primary Secondary Amine (PSA), 10 mg Graphitized Carbon Black (GCB), and 600 mg anhydrous magnesium sulfate. After vigorous shaking for a minute, the tube was centrifuged at 3000 rpm for 10 min. Four ml of supernatant was transferred to a turbovap tube, which was then evaporated to dryness and the residue was reconstituted with 1 mL acetonitrile. This extract was transferred into a 1.5 mL glass auto-sampler vial for LC–MS/MS analysis after filtering through a 0.2 µm filter membrane. Water samples were extracted by liquid–liquid partitioning using dichloromethane (DCM). Briefly, 200 mL water was added to 500 mL separating funnel containing 10 g sodium chloride and shaken well. For separation of DCM layer, 50 mL DCM was added to the funnel and was shaken well for 1 min. The aqueous layer was repeatedly extracted with 50 mL DCM and all the DCM layers were pooled together and dried using anhydrous sodium sulfate. The dried layer was finally reconstituted to 1 mL with acetonitrile and filtered through a 0.2 µm filter membrane before the extract was transferred into a 1.5 mL glass auto-sampler vial for LC–MS/MS analysis.

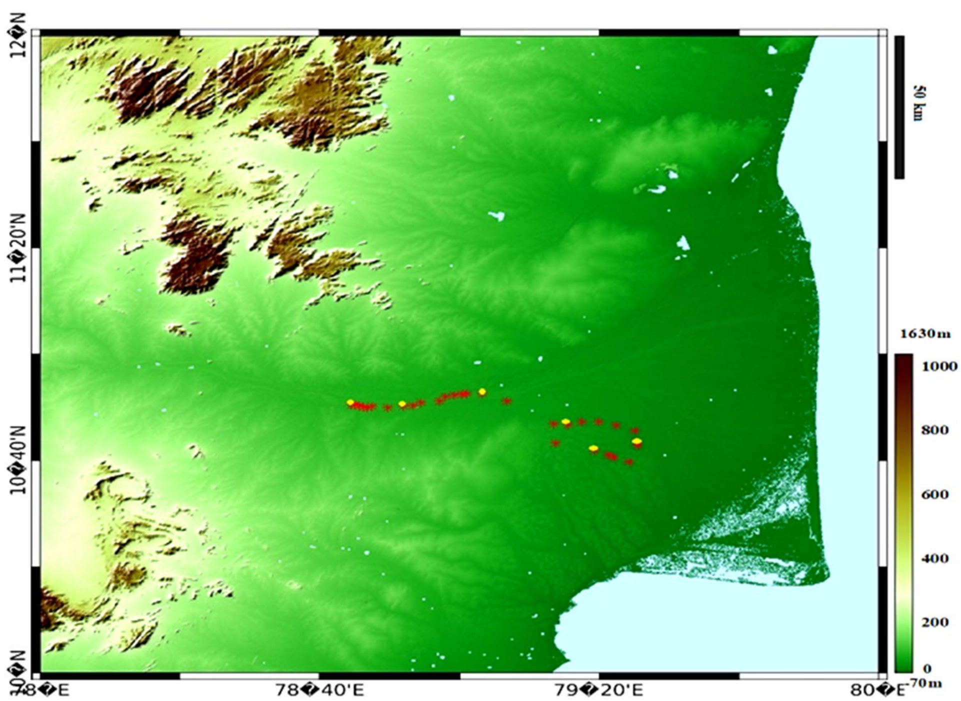

Fig. 1 Study area map highlighting the locations of sampling

Quantification was performed in Waters LC/MS/MS, positive ESI mode with a C18, 5 µm (4.6 × 250 mm) column. The mobile phase consisted of acetonitrile: water (50:50) with 0.5% formic acid. A Tandem Quadrupole Detector (TQD) Acquity (Waters, USA) with Electrospray Ionization Interface (ESI) was used for the confirmation of the analyte. The analytes in a chromatogram were identified based on the retention time, precursor/product ion combination (Table 1 and Fig. 2). The standardized instrument conditions were source temperature at 150°C, capillary voltage at 3.5 kV, optimum column temperature at 30°C, and desolvation temperature at 500°C, desolvation gas flow at 1100 L/h, cone gas flow at 50 L/h, and the collision gas flow at 0.18 mL/minute. The flow rate was set at 0.5 mL/minute with an injected volume of 10 µL and working standards of 0.5 and 1.0 µg/mL were used. The calibration curves were obtained using standard solutions at 0.025, 0.055, 0.075, and 0.1 ppm (Fig. 3). Recovery assay was conducted at three levels of fortification at 0.05, 0.25, 0.5 ppm for soil and 0.0025, 0.005, and 0.01 ppm for water, with an acceptable range of recovery between 70–120%, with relative standard deviation at RSD < 20%. The Limit of Detection (LOD) and the Limit of Quantification (LOQ), values for water and soil were 0.001 ppm and 0.0025 ppm and 0.025 ppm and 0.05 ppm respectively. The physicochemical properties of the experimental soil were (Mean ± SD), pH (7.83 ± 0.74), electrical conductivity (0.22 ± 0.07 dS/m), water holding capacity (71.8 ± 16.81%), and bulk density (1.65 ± 0.11 g/cm^3).

Table 1 Precursor ion, product ion, recovery % and linearity of neonicotinoids in LC–MS/MS

Insecticide	Precursor ion m/z	Product ion m/z	Recovery (%)	R^2 value calibration curve
Imidacloprid	256.132	209.146	70–120	> 0.989
Acetamiprid	223.160	126.115	70–120	> 0.989
Thiacloprid	253.096	126.126	70–120	> 0.989
Clothianidin	250.104	169.108	70–120	> 0.989
Thiamethoxam	292.168	211.109	70–120	> 0.989

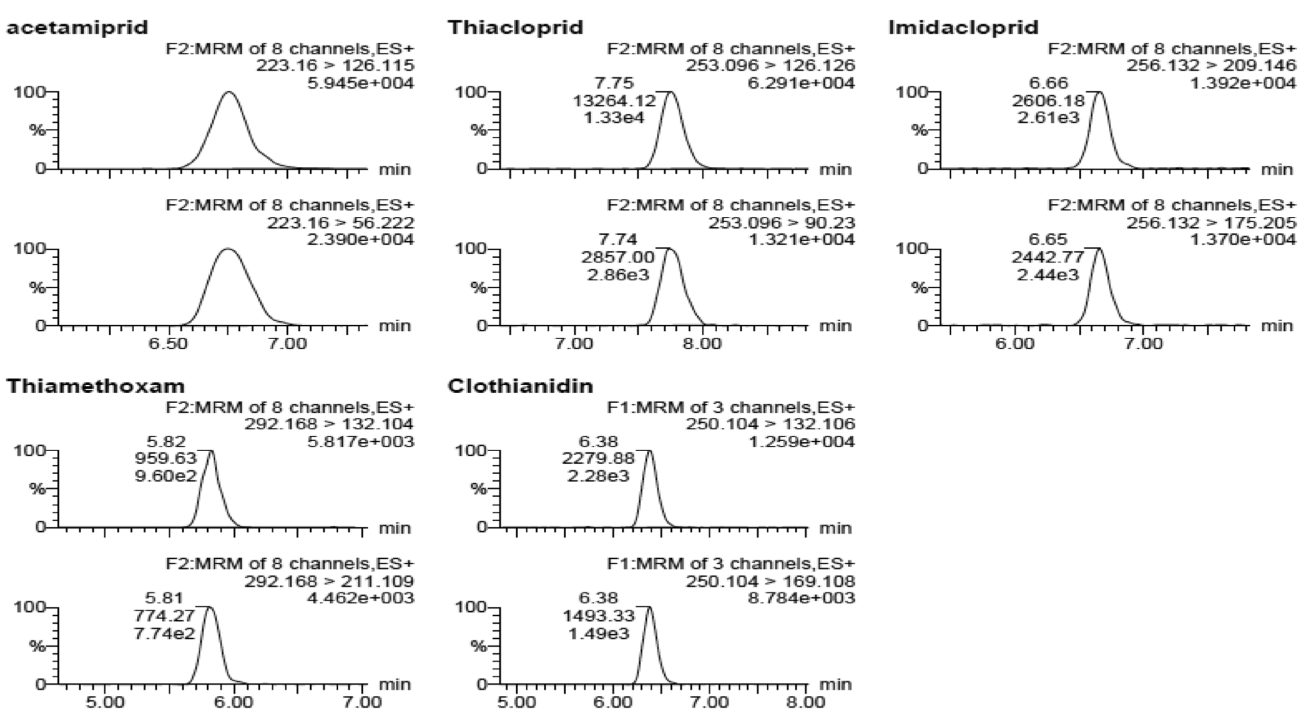

Fig. 2 LC–MS/MS chromatogram of standards in soil

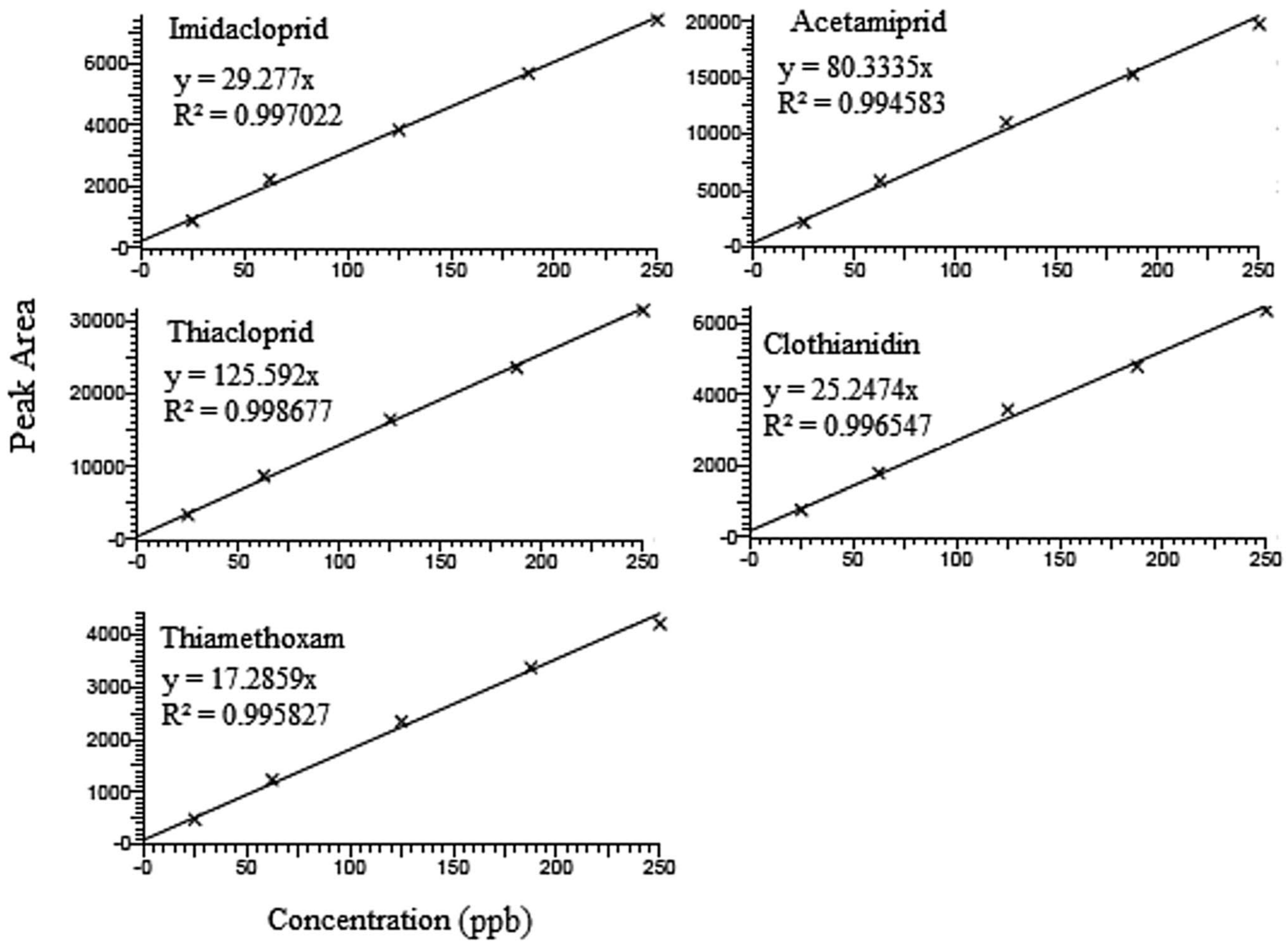

Fig. 3 Calibration curves of neonicotinoids in water

Results and Discussion

Although the Cauvery delta region is a protected agricultural zone, short-duration rice varieties and increased pest infestations have led to the extensive use of pesticides along this region. The results of the study found no detectable residues at concentrations above LOD in the water-soil systems. The standard curves demonstrated good linearity for calibration curves ($r^2 > 0.989$) (Fig. 3). The average retention time of acetamiprid, thiacloprid, imidacloprid, thiamethoxam, and clothianidin in water and soil were 6.61 ± 0.03, 7.66 ± 0.03, 6.68 ± 0.05, 5.70 ± 0.06, 6.31 ± 0.05 and 6.87 ± 0.16, 6.26 ± 3.07, 6.66 ± 0.03, and 5.84 ± 0.42, 6.63 ± 0.24 respectively.

The Cauvery delta region experiences a mean annual temperature of 28°C while soaring up to 43°C in summer. The high elevated temperatures and the prolonged exposure of the top agricultural soil to UV radiations readily results in photolytic degradation, thus preventing their accumulation and load (Op de Beeck et al. 2017). Further, the higher microbial activity in the delta soil also facilitates rapid microbial degradation of the residues (Sabourmoghaddam et al. 2015). Few studies on neonicotinoids from the United States during 1999–2015 showed detection frequencies below 20% (Craddock et al. 2019). Similarly, soil samples collected from 25 commercial fields exposed to seed treatments in southwestern Ontario, Canada recorded a mean neonicotinoid residue of 5.59 ng/g in the parent soil and 71.17 ng/g in the soil dust (Limay-Rios et al. 2016). A Canadian study by Schaafsma et al. (2015) reported residues of clothianidin and thiamethoxam in 100 and 98.7% of the water samples associated with maize production. Numerous studies have also shown variable concentrations of neonicotinoids in surface waters. Long-term water monitoring studies have reported neonicotinoid contamination for average surface water at 0.13 µg/l (n = 19) (Morrissey et al. 2015), while wetlands surrounded by agricultural fields reported arithmetic mean concentrations at 0.007 µg/L (Smalling et al. 2015). Likewise, the average imidacloprid concentrations in seven streams at Eastern Hemlock forests were reported at 0.067 µg/L (Benton et al. 2016), while in maize fields the average concentration of clothianidin in groundwater was recorded at 0.060 µg/L (de Perre et al. 2015). A study by Schaafsma et al. (2015) reported arithmetic mean residues of clothianidin at 0.002 µg/L and thiamethoxam at 0.001 µg/L in surface water around the maize fields in Canada. In yet another study, thiamethoxam was recorded in pollen and nectar of wildflowers of *Heracleum sphondylium* and *Papaver rhoeas* at 86 ng/g and 64 ng/g respectively (Botias et al. 2016). Some studies have also reported higher residues of neonicotinoids in agricultural fields coinciding with higher precipitation rates (Hladik and Kolpin 2016; Wood and Goulson 2017).

In the present study, the hydropedological characteristic of the soil aids in delta filtration, thus straining the degraded pollutants from the agricultural soil (Giorio et al. 2017; Dragon et al. 2019). The saturated delta soil and higher water solubility of the neonicotinoids enhance the leaching rate of the pollutants formerly degraded by photolysis and microbial activity. Higher leaching results in dispersion, followed by rapid vertical migration and infiltration. Since the farmers in the delta region depend on the monsoon for cultivation and during this time the soil is saturated, migration is high. During the wet periods, the leaching is maximized, and the pesticides rapidly percolate into the underground water table. The long-wet season of the delta region also facilitates this migration, thus recording less persistence of the residues in the given environmental matrix. Since the underground water resources are shielded from photolysis, the residues accumulate in the groundwater threatening human life (Op de Beeck et al. 2017). Only limited studies are available on groundwater contamination by neonicotinoids (Mineau and Palmer 2013; Mineau 2019; Blanchoud et al. 2019). Hence, research incorporating pesticide fate models are essential to determine the degradation process and infiltration rate of neonicotinoids, followed by their persistence in the groundwater to divulge the scientific gaps.

Conclusion

The study infers that the persistence and migration of pesticides vary based on the agro-climatic characteristics of the region and the hydropedological conditions of the water-soil systems. Hence, it is essential to determine the counteracting environmental processes and the pathways that facilitate rapid degradation. Given that these compounds can easily be mobilized into the environment, the below LOD values illustrate the effectiveness of pesticide removal by delta filtration, which needs further research. However, our study raises the concern of possible vertical migration and infiltration of the residues into the soil aquifers that may contaminate the groundwater resources. Since the Cauvery delta region is the rice bowl of South India, this region needs frequent monitoring of any residual contamination in both the agricultural matrix and groundwater resources.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00128-021-03233-4.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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